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# Organometallic Chemistry

## Electrochemically induced formation of organomercury compounds
## 1. A system containing metallic mercury, (dimethylglyoximato)cobalt(II), and butyl bromide

*R. D. Rakhimov, E. R. Milaeva, O. V. Polyakova, and K. P. Butin**

*Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory,*
*119899 Moscow, Russian Federation.*
*Fax: +7 (095) 939 5546*

A procedure for the alkylation of metallic mercury by (dimethylglyoximato)butylcobalt(III) electrochemically generated in the presence of butyl bromide is proposed.

**Key words:** metallic mercury, butylmercury salts, (dimethylglyoximato)cobalt, alkylating agents, electrochemical synthesis.

The mechanism of the chemical transformation of various compounds into alkylmercury salts or dialkylmercury has been intensely studied in connection with the problem of environmental contamination by alkylmercury salts (usually, methylmercury salts). The detailed mechanism of biological alkylation is not yet clear.[1]

The discovery in 1968 (see Ref. 2) that methylcobalamine-containing methanogenic bacteria can methylate inorganic mercury salts in natural deposits made it possible to study the kinetics and mechanism of methylation of inorganic mercury by methylcobalamine ($CH_3Co^{III}B_{12}$) and by other methylcobalt chelate complexes, $MeCo^{III}$(chel) that model vitamin $B_{12}$.

The following chelating equatorial ligands, in which nitrogen and less commonly oxygen atoms served as the donors of lone electron pairs were used: dimethylglyoximato and its borofluoride derivative, bis(salicylidene)ethylenediamine dianion, acetylacetone and ethylenediamine Schiff's base dianion, the macrocyclic ligand 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, and others (see Ref. 1). It was established that transfer of methyl from the Co at Hg occurred via electrophilic attack by $Hg^{2+}$ at the methyl bound to Co:

$$\mathrm{MeCoB_{12}} + \mathrm{HgX_2} \xrightarrow[\mathrm{Solv}]{S_E2} \mathrm{MeHgX} + [\mathrm{SolvCoB_{12}}]^+ + \mathrm{X}^-.$$

The rate of methyl transfer depends on the nature of $X^-$ and decreases in the series:[3]

$$X = AcO^- \gg Cl^- \sim SCN^- \sim Br^- \gg CN^-.$$

The chromium(III) complex, $[MeCr(chel)(H_2O)]^{2+}$ (chel is 15-membered cycle with four nitrogen atoms), which very rapidly methylates $Hg^{2+}$ (see Ref. 4), is a remote analog of methylcobalamine.

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It was shown that methylcobalt compounds with a great variety of chelate-forming ligands can serve as carriers of an alkyl group to mercury, and the transfer of an alkyl group can occur not only from cobalt, but from other metals as well. Complexes of metals that form sufficiently stable σ-bonded alkyl—metal compounds are promising for investigation. For example, for porphyrin complexes, these metals are Fe, Ru, Co, Rh, Ir, Ti, Al, Ge, Ga, Sn, and Zn,[5] and probably, Ni, which is a component of the F430 coenzyme of methanogenic bacteria.[2]

To get insight into the mechanism of the formation of methylmercury in the environment, not only must the reactions of inorganic mercury with organometallic complex-carriers of an alkyl group be studied, but the formation of the carrier itself from a simpler complex without the alkyl—metal bond and an appropriate alkylating reagent must also be studied.

An anionic complex of univalent cobalt $[Co^{I}(chel)]^{-}$ must act as the nucleophilic agent, for example, in the reaction with alkyl halide, to produce an alkyl carrier (an electroneutral complex $RCo^{III}(chel)$):

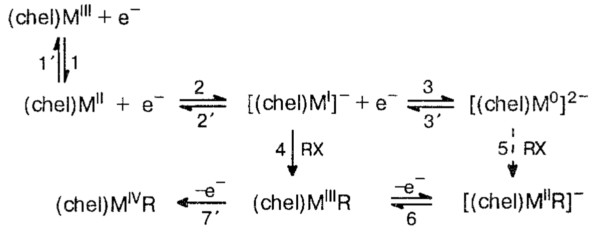
$$R{-}X \; + \; [Co^{I}(chel)]^{-} \; \rightarrow \; R{-}Co^{III}(chel) \; + \; X^{-}.$$

These complex anions have been fairly well studied. Owing to their ability to react rapidly with alkylating reagents they are named "supernucleophiles".[6,7] For example, in Pearson's scale[8] the parameter of nucleophilicity of $Co^{I}$ complexes ($n = \log(k/k_0)$, where $k$ and $k_0$ are second-order rate constants for the $S_N2$-reaction of MeI with a given nucleophile and the metal, respectively) equals 12—14, whereas for such strong nucleophiles as $I^{-}$ or $CN^{-}$, $n = 7$. Similarly, the complex anion, octaethylisobacteriochlorine ($Ni^{I}$ (a supernucleophile)[9]) reacts with alkylating reagents ~$10^4$ times faster than the $PhS^{-}$ anion (a strong nucleophile).

Anionic complexes with supernucleophilic properties can be obtained electrochemically from the corresponding complexes of metals in higher oxidation states. When an alkylating reagent is added to an electrochemical cell, peaks corresponding to the formation of the alkylation product can be observed on voltammograms. In works carried out during the past 15 years, the possibility of electrochemical alkylation of transition metals was shown for macrocyclic complexes of iron,[10—13] rhodium,[14] and cobalt,[15,16] as well as for derivatives of vitamin $B_{12}$ (see Refs. 16, 17).

The sequence of the reactions occurring on the surface of the electrode and in the solution, can be represented by the general Scheme 1. For iron complexes, alkylation occurs both in the $Fe^{I}$ and the $Fe^{0}$ states and in both cases $[(chel)Fe^{II}R]^{-}$ is the reaction product owing to the disproportionation $Fe^{III}R + (Fe^{I})^{-} \rightarrow [Fe^{II}R]^{-} + Fe^{II}$. The reduction of cobalt and rhodium porphyrin complexes and vitamin $B_{12}$ derivatives terminates in the formation of $[(chel)M^{I}]^{-}$, which enters an $S_N2$-reaction with alkyl halides. As a result of this reaction, cyclic voltammograms (CVA) show that in the presence of alkyl halide there is a new cathodic peak corresponding to process 6, which occurs at more cathodic potentials than process 2.

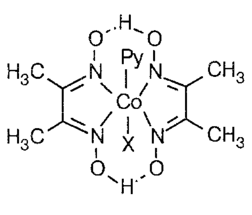
**Scheme 1**



The aim of this work is to study the electrochemically induced formation of organomercury compounds in a system that simultaneously contains metallic mercury, a chelate nonalkylated $Co^{II}$ complex, and an alkylating reagent, by potential scanning over a wide range of cathodic and anodic regions. The $Co^{I}$ supernucleophile, which can be alkylated, is generated in the cathodic region. In the anodic region, metallic mercury is dissolved to form $Hg^{2+}$ cations, the acceptors of alkyl carbanions. If this process occurs sufficiently fast in the characteristic time-scale of CVA, then during repeated scanning of the cathodic region one can expect the appearance of new peaks caused by the reduction of alkylmercury salt.

## Experimental

The starting cobalt compound, bis(dimethylglyoximato) cobalt containing two axial pyridine ligands, was synthesized by the known procedure.[18] The corresponding butyl derivative, $BuCo(DH)_2Py$, was also synthesized by the known procedure.[19]



$Co(DH)_2Py_2$; X = Py

$BuCo(DH)_2Py$; X = $Bu^n$

*n*-Butyl bromide was chosen as the alkylating reagent. Acetonitrile purified by the known procedure[20] served as the solvent, and a 0.05 *M* solution of $Bu_4NBF_4$ was used as the background electrolyte.

Polarization curves were recorded on a PA-2 polarograph, which allows one to abruptly change the direction of scanning. The potential was measured relative to Ag/AgCl/KCl sat. To create the mercury film electrode, a platinum electrode was kept for 10 min at a potential of −1.00 V in a solution containing $Hg(OAc)_2$.

## Results and Discussion

$Co(DH)_2Py_2$ can be both oxidized and reduced. Its oxidation is reversible ($E_{pa}$ = 1.22 V; $E_{pa} - E_{pc}$ = 0.07 V; $i_{pc}/i_{pa}$ = 0.8). The reversibility of the process seems to attest that the $Co^{II}/Co^{III}$ transition takes place during oxidation.

The reduction occurs in two one-electron stages. The first stage is reversible ($E_{pc}$ = −1.17 V; $E_{pc} - E_{pa}$ = 0.09 V; $i_{pa}/i_{pc}$ = 1), and the second is quasi-reversible (EC-mechanism). The second stage of the reduction is likely to be responsible for the electron transfer to the π-system of pyridine, and the first stage corresponds to the $Co^{II}/Co^{I}$ transformation. When $Bu^nBr$ ($5 \cdot 10^{-3}$ *M*) is added to the solution under study, which contains $1 \cdot 10^{-3}$ *M* $Co(DH)_2Py_2$, a new cathodic peak (Fig. 1, peak C) appears on the CVA curve and the height of the anodic peak, which corresponds to the $Co^{I}/Co^{II}$ transition, decreases simultaneously. The new cathodic peak corresponds to the formation of $BuCo^{III}(DH)_2Py$ in reaction 4 (see Scheme 1).

Chemically synthesized $BuCo(DH)_2$ is reduced at the potential $E_{pc}$ = −1.69 V (EC-mechanism), which is very close to the potential of peak C, which appears when $Bu^nBr$ is added.

The interaction of the alkyl complex formed upon electrochemical activation with mercuric ions was studied by the following procedure: a mercury film electrode was kept in a solution of $Co(DH)_2Py_2$ at −1.30 V for 5 min to consume the alkyl product. Then the potential of +0.60 V, at which the oxidation of metallic mercury on the surface of the platinum electrode begins, was established. Next, multiple scanning of the potential from +0.6 to −1.3 V and back was performed. During the scanning two peaks (Fig. 2, peaks B and C) with $E_{pc}$ = −0.46 and −0.70 V appeared on the CVA cathodic curve in addition to the peak of the reduction of $Hg^{II}/Hg^0$ (Fig. 2, peak A) and the peak of the reduction

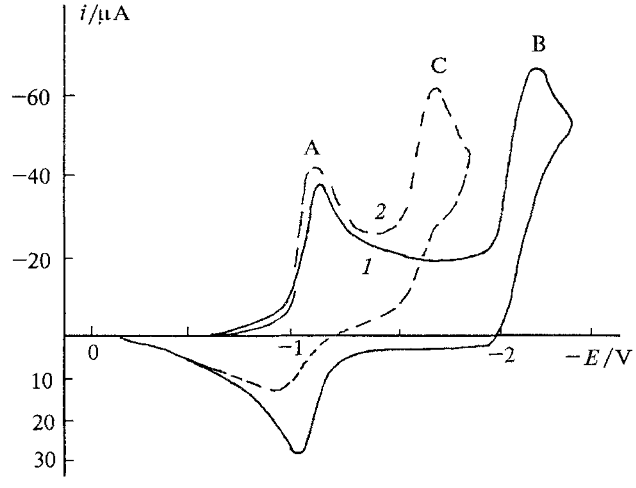


**Fig. 1.** Cyclic voltammograms of $Co(DH)_2Py_2$ ($1 \cdot 10^{-3}$ *M*) (*1*) and $Co(DH)_2Py_2$ in the presence of $5 \cdot 10^{-3}$ *M* $Bu^nBr$ (*2*).

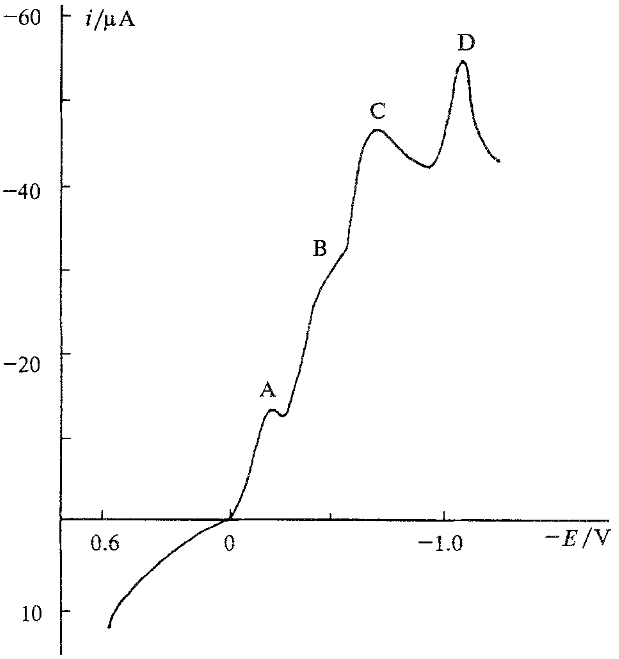


**Fig. 2.** Cathodic branch of the CVA curve observed during the potential scanning from +0.6 to −1.3 V and back ($1 \cdot 10^{-3}$ *M* $Co(DH)_2Py_2$ and $5 \cdot 10^{-3}$ *M* $Bu^nBr$ in MeCN containing 0.05 *M* $Bu_4NBF_4$, 20 °C).

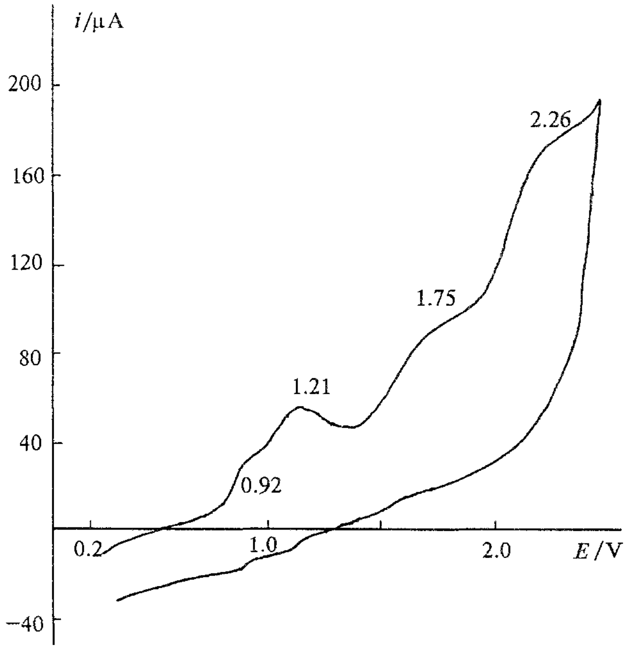


**Fig. 3.** Cyclic voltammogram after 20-h storage of a solution of $BuCo(DH)_2Py$ ($1 \cdot 10^{-3}$ *M*) and $Hg(OAc)_2$ ($5 \cdot 10^{-3}$ *M*) in MeCN containing 0.05 *M* $Bu_4NBF_4$ at 20 °C.

of the initial complex (peak D). According to our data, BuHgBr is reduced at these potentials.

When an acetonitrile solution containing $BuCo^{III}(DH)_2Py$ ($1\cdot10^{-3}$ *M*) and $Hg(OAc)_2$ ($5\cdot10^{-3}$ *M*) was kept for 20 h, four peaks at potentials 0.92, 1.22, 1.75, and 2.26 V, responsible for the oxidation of $BuCo(DH)_2Py$, $Co(DH)_2Py_2$, $Bu^nHgOAc$, and $Hg(OAc)_2$, respectively (Fig. 3), were observed on the anodic polarization curve.

Thus, (dimethylglyoximato) butylcobalt is a carrier of alkyl groups to inorganic mercury.

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